Claims

1. A thermosetting composition comprising crosslinked polymer microparticles with a size of between 10 and 200 nm, characterized in that said microparticles are at least partially soluble, miscible and/or dispersible in the starting thermosetting composition and carry at least one reactive functional group which can react with at least one reactive functional group carried by at least one of the reactive components of the thermosetting composition and in that the thermosetting composition is selected from the compositions of type: epoxy/amine, epoxy/anhydride, isocyanate/amine, isocyanate/alcohol, unsaturated polyesters, vinyl esters, unsaturated polyester and vinyl ester blends, unsaturated polyester/urethane hybrid resins, polyurethane-ureas, reactive dicyclopentadiene resins or reactive polyamides.

2. The composition as claimed in claim 1, characterized in that the microparticles carry at least one second reactive functional group distinct from the first which can react with at least one other functional group of the same type carried by another microparticle and/or by at least one reactive component of the thermosetting composition.

3. The composition as claimed in either of claims 1 and 2, characterized in that the microparticles carry at least one functional group which reacts by a polycondensation reaction and at least one second functional group which is an α,β-ethylenic unsaturation which can polymerize by the radical route or by a specific reaction.

4. The composition as claimed in one of claims 1 to 3, characterized in that said microparticles are obtained by polymerization in dispersion in a nonaqueous medium which is not a solvent of the polymer formed, starting from a composition comprising

ethylenically unsaturated polymerizable compounds comprising:

- at least one monomer A, comprising a single ethylenic unsaturation which can polymerize by the radical route, conferring, on the microparticles formed in said nonaqueous medium, self-stabilization during and after polymerization, without any addition of polymer having a role of stabilizing agent, either before or during or after polymerization,
- at least one compound B comprising at least two ethylenic unsaturations which can polymerize by the radical route,
- at least one compound C other than A or B and comprising at least one ethylenic unsaturation which can polymerize by the radical route and at least one second reactive functional group f1 other than an ethylenic unsaturation,

and optionally at least one compound D, other than A, comprising a single ethylenic unsaturation which can polymerize by the radical route.

5. The composition as claimed in claim 4, characterized in that the compounds A have a general formula (I):

$CH_2=CR_1-X-(R_2-Y)_k-R$ (I)

with R_1 = H or CH_3,

X = ester $-(C=O)O-$ or amide $-(C=O)N(R_3)-$,

Y = ester $-O(O=C)-$, amide $-(R_3)N(C=O)-$ or urethane $-O(O=C)NH-$,

R_2 = C_2-C_6 alkylene radical, which can be substituted by functional groups, such as OH,

R_3 = C_1-C_6 alkyl or H,

k = 0 or 1,

R = linear or branched C_8-C_{22} alkyl or alkenyl radical or aralkyl radical substituted on the aromatic ring with a C_8-C_{22} group or substituted or unsubstituted C_6-C_{22} mono- or polycyclic radical, which can comprise an f2 reactive functional group selected from:

carboxylic acid or anhydride, hydroxyl, epoxy, isocyanate or silane.

6. The composition as claimed in one of claims 1 to 3, characterized in that said microparticles are obtained by polymerization of a composition comprising ethylenically unsaturated polymerizable compounds composed of:

- a first component A' which represents from 50 to 99 mol% of said composition comprising polymerizable compounds and which is composed of isobornyl and/or norbornyl and/or cyclohexyl and/or lauryl and/or tridecyl and/or octadecyl and/or Cardura E10 (meth)acrylate, optionally in combination with a C_2-C_8 alkyl (meth)acrylate,
- a second component B' composed of at least one monomer or oligomer comprising at least two ethylenic unsaturations which can polymerize by the radical route,
- a third component C' composed of at least one monomer or oligomer comprising, in addition to an ethylenic unsaturation which can polymerize by the radical route, at least one second reactive functional group f1' other than the ethylenic unsaturation,

with the possibility of at least partial chemical modification of the f1' starting functional groups to f2' final functional groups, provided that the f1' functional groups selected do not react with one another during the polymerization and provided that the sum of the three polymerizable components A'+B'+C' is equal to 100 mol%.

7. The composition as claimed in claim 6, characterized in that the microparticles carry f1' functional groups, contributed by the third component C', selected from: epoxy, hydroxyl, carboxyl, carboxylic anhydride, isocyanate, silane, amine or oxazoline, and, if appropriate, f1' functional groups at least partially modified to f2' functional groups

selected from: (meth)acrylates, vinyls, maleates, maleimides, itaconates, allyl alcohol esters, dicyclopentadiene-based unsaturations, unsaturated C_{12}-C_{22} fatty esters or amides, carboxylic acid salts or quaternary ammonium salts.

8. The composition as claimed in one of claims 1 to 7, characterized in that the level of reactive crosslinked microparticles lies between 0.5 and 50% by weight with respect to the overall organic thermosetting composition.

9. The composition as claimed in one of claims 1 to 8, characterized in that the thermosetting composition is based on epoxy/amine and comprises:

a) at least one epoxide-comprising compound, having a functionality with regard to epoxy groups of at least two, with an aromatic and/or (cyclo)aliphatic structure,

b) at least one amine compound, with an amine functionality of at least two, with an aromatic and/or (cyclo)aliphatic structure,

c) if appropriate, a monofunctional epoxide compound carrying a second distinct functional group which can polymerize by the radical route,

d) 0.5-50% by weight with respect to a) + b) + c) + d) of reactive crosslinked microparticles as defined in one of claims 1 to 8.

10. The composition as claimed in claim 9, characterized in that the reactive crosslinked microparticles carry at least one epoxy or carboxylic acid or anhydride functional group.

11. The composition as claimed in claim 10, characterized in that said microparticles can be obtained by polymerization starting from:

i) 10-50 mol% of lauryl and/or tridecyl and/or octadecyl and/or docosyl and/or isobornyl and/or Cardura E 10 (meth)acrylate,

14. The composition as claimed in one of claims 1 to 8, characterized in that the thermosetting composition comprises:

a) at least one unsaturated polyester and/or at least one unsaturated polyester modified by a polyisocyanate and/or at least one vinyl ester,

b) at least one copolymerizable comonomer carrying at least one α,β-ethylenic unsaturation chosen from vinylaromatic and/or (meth)acrylic and/or allyl monomers,

c) optionally at least one second monomer carrying at least two reactive functional groups, one of which can polymerize by the radical route and the other by a condensation reaction,

d) 0.5-50% and preferably from 5 to 25% by weight of reactive crosslinked microparticles as defined in one of claims 1 to 7.

15. The composition as claimed in claim 14, characterized in that said microparticles carry at least one (meth)acrylate or hydrogen maleate functional group.

16. The composition as claimed in claim 15, characterized in that said microparticles can be obtained by a first polymerization stage starting from:

i) 10-40 mol% of Cardura E10 (meth)acrylate,

ii) 10-75 mol% of butyl and/or tert-butyl and/or 2-ethylhexyl and/or 2-(2-ethoxyethoxy)ethyl (meth)acrylate and of styrene, with a molar ratio of styrene to (meth)acrylic monomers varying from 0 to 0.2,

iii) 5-40 mol% of hydroxyethyl (meth)acrylate or of maleic anhydride or of (meth)acrylic acid or of glycidyl methacrylate,

iv) 2-10 mol% of hexanediol and/or propylene glycol and/or neopentyl glycol and/or trimethylolpropane (meth)acrylate,

with the sum of the molar percentages of all these constituents i)+ii)+iii)+iv) being equal to 100,

followed by a second stage of at least partial chemical modification of the starting reactive functional groups according to:

- the starting hydroxyl functional groups to hydrogen maleates by reaction with maleic anhydride and/or to (meth)acrylates by reaction with (meth)acrylic acid,
- the starting epoxy functional groups to (meth)acrylates by reaction with (meth)acrylic acid,
- the acid functional groups to methacrylate by reaction with glycidyl methacrylate,
- the anhydride functional groups to (meth)acrylates and residual acids by reaction with a hydroxyethyl or hydroxypropyl (meth)acrylate or with glycidyl methacrylate.

17. The use of the composition as defined in one of claims 1 to 16 in coatings.

18. The use as claimed in claim 17, characterized in that said coatings are protective coatings for electrical or electronic components, items or devices.

19. The use of the composition as defined in one of claims 1 to 16 for the manufacture of molded items and of items made of composite materials.

20. A thermoset matrix obtained from the thermosetting composition as defined in one of claims 1 to 16.

21. A protective coating, molded item or item made of composite materials obtained from the thermosetting composition as defined in one of claims 1 to 16.